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**IMPROVED UNIFORMITY OF PHOTOCATHODE SENSITIVITY**

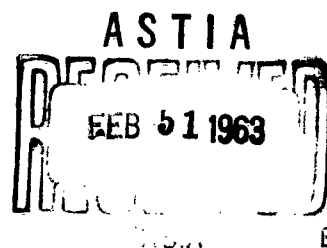
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(Prepared under Contract No. AF33(616)-8303  
by Radio Corporation of America, Lancaster, Pa.  
Authors: A. H. Sommer, R. E. Simon and B. H. Vine)



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## **FOREWORD**

This report was prepared by Radio Corporation of America, Electron Tube Division, Lancaster, Pennsylvania, on Air Force Contract AF33(616)-8303, under Task No. 415605 "Special Tubes," of Project No. 4156, "Electronic Tube Technology." The work was administered under the direction of Electronic Technology Laboratory, Aeronautical Systems Division. The sponsoring office was ASRNET-2. Mr. Bilyie E. Rambo was project engineer for the Laboratory.

The studies presented began in May 1961, and were concluded in May 1962. Dr. A. H. Sommer was responsible for the research activity of the Radio Corporation of America.

The chief contributors were Dr. A. H. Sommer, Dr. R. E. Simon and Dr. B. H. Vine.

This report is the Final Report and it concludes the work on Contract AF33(616)-8303.

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#### ABSTRACT

The objective of this work was to gain a better understanding of the parameters determining the photoelectric sensitivity of multi-alkali photocathodes. An improved understanding should lead to practical improvements, in particular greater reproducibility of the activation process, greater uniformity over the cathode area, higher quantum efficiency, longer threshold wavelength, etc. The studies to be reported cover three approaches. First, an attempt was made to eliminate the effect of contaminating gases set free during the release of alkali metals in the later stages of the activation process. Second, the effect of systematic modifications of the cathode activation procedure, such as sequence of the processing stages, thickness of the Sb base layer, superficial oxidation, etc., were investigated. Third, a molecular beam technique was developed for Cs which made it possible to study the effect on the photocathode of the extremely small quantities of Cs which correspond to a fraction of a monatomic layer.

#### PUBLICATION REVIEW

Publication of this Technical Documentary Report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

  
WILLIAM H. NELSON

Chief, Sensor and Display Section  
Thermionics Branch  
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ASD-TDR-62-619

## TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
I. PROBLEMS OF MULTI-ALKALI ACTIVATION	2
II. ACTIVATION PROCESS EXPERIMENTS	5
A. Tube Design	5
B. Attempts to Produce Clean Alkali Metals	6
a. New Cesium Generators	6
b. Pre-flashing of Alkali Metal Generators	6
C. Effect of Oxygen on Multi-Alkali Cathodes	8
D. Activation Process with Predetermined Amounts of Antimony	10
E. Modification of the Cesium Process	11
III. MOLECULAR BEAM EXPERIMENTS	12
A. Introduction	12
B. The Cesium Beam Technique	15
a. General Considerations Concerning Atomic Beams	15
b. Tube Designs for Cs Beam Experiments	17
C. Experimental Results	18
a. Introductory Remarks	18
b. Calibration of Cs Beam	18
c. Problems of Sb Evaporation	19
d. Processing of Cs <sub>3</sub> Sb Cathodes with Cs Beam	20
e. Second Type Cs Beam Tube	22
f. Processing of Na <sub>2</sub> KSb Cathodes with Cs Beam	23
g. Processing of Cs <sub>3</sub> Sb Cathodes in an Enclosed Chamber	23

## TABLE OF CONTENTS (CONT'D.)

	<u>Page</u>
IV. MISCELLANEOUS EXPERIMENTS AND NOTES	24
A. On Evaporated Alkali Metal Generators	24
B. Vapor Pressure Considerations	25
C. Monitoring Problem	26
D. Electron Diffraction	26
V. SUMMARY AND CONCLUSIONS	27
BIBLIOGRAPHY	37

## LIST OF ILLUSTRATIONS

	<u>Page</u>
Fig. 1    Experimental Tube for the Study of Photo-cathode Activation	29
Fig. 2    Experimental Tube for Activating Photo-cathodes with an Atomic Beam of Cesium	30
Fig. 3    Number of Cs Atoms in Atomic Beam as a Function of Temperature	31
Fig. 4    Experimental Tube to Measure the Relation between Thickness and Light Transmission of an Evaporated Antimony Film	32
Fig. 5    Light Transmission of An Evaporated Sb Film as a Function of Thickness	33
Fig. 6    Experimental Tube for the Activation of $\text{Cs}_3\text{Sb}$ Cathodes in an Enclosed Chamber	34
Fig. 7    Cesium Beam Tube, Second Type	35
Fig. 8    Temperature	36
Fig. 9    Vapor Composition	36

## INTRODUCTION

The basic aim of the experimental work carried out under this Contract was to study and, if possible, overcome the causes of non-uniformity of individual multi-alkali photocathodes and of the non-reproducible sensitivity of cathodes made by conventional activation processes. In the course of the work, two approaches to the stated objective seemed to hold out the greatest promise and complemented each other.

One approach consisted of systematic modifications of the conventional activation process of multi-alkali cathodes. Since the cathode contains four chemical elements and has to be made by a processing schedule consisting of many separate steps, it is reasonable to expect that the optimum schedule has not yet been discovered. Moreover, the modifications should yield useful information as to the relative importance of the successive steps and their sequence.

The second approach was of an analytical nature. Attempts were made to correlate photoelectric characteristics with the absolute and relative amounts of the three alkali metals contained in the cathode. As will be shown, the most promising technique for this aspect of the work has turned out to be the molecular beam method, supplemented by more conventional chemical analysis.

The main part of this report will be subdivided into three sections: Section I will summarize the problems associated with the fabrication of multi-alkali photocathodes. Section II will describe the results of modified activation procedures. Section III will deal with the molecular beam experiments.

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## I. PROBLEMS OF MULTI-ALKALI ACTIVATION

The following discussion will be confined to semitransparent cathodes, i. e., to cathodes which are illuminated from the substrate interface as distinct from cathodes where the light is incident from the vacuum interface. This type of cathode, because of its greater optical and electron-optical efficiency, is required for most tubes of technical importance, such as multipliers, image tubes, etc. For semitransparent cathodes, the thickness is very critical because light is lost by transmission if the cathode film is too thin and photoelectrons are lost if the film is so thick that an appreciable number of electrons is produced at distances from the vacuum interface greater than the escape depth.

The special problems associated with the processing of multialkali cathodes are best understood by comparing this cathode with the simpler cesium-antimony ( $\text{Cs}_3\text{Sb}$ ) cathode. The  $\text{Cs}_3\text{Sb}$  cathode is made essentially in two steps. First, a thin Sb layer is deposited by evaporation. The optimum thickness of the Sb film is obtained by monitoring the light transmission of the film and discontinuing evaporation at a value (around 85%) known from past experience (see, for instance, Ref. 1) to produce cathodes of highest sensitivity. In the second step, the Sb film is exposed to Cs vapor at a temperature of approximately  $150^\circ\text{C}$  at which reaction takes place immediately. During the reaction, the photoemission increases and goes through a peak when the composition corresponds to the stoichiometric formula  $\text{Cs}_3\text{Sb}$  (Ref. 2). Any Cs introduced in excess over this ratio is not chemically bound (Ref. 2) and is rapidly removed by baking. The two essential points here are, first, that the amount of Sb in the final cathode can be exactly predetermined (at least within the accuracy with which the relation between thickness and light transmission is valid) and, second, that the amount of Cs introduced is not critical because an excess over the optimum amount can easily be removed. Thus it is apparent why it is relatively simple to make  $\text{Cs}_3\text{Sb}$  cathodes in large numbers and with reasonably uniform photoemissive properties.

In contrast to the  $\text{Cs}_3\text{Sb}$  cathode, the most successful process at present available for the activation of the multi-alkali cathode does not allow the use of a predetermined amount of antimony nor does it provide a simple method of adjusting the content of alkali metal to an optimum amount. To explain these differences, it is necessary to describe

briefly the processing of a multi-alkali cathode.

It is known (Ref. 3 ) that the composition of the material of highest sensitivity corresponds to the formula  $\text{Na}_2\text{KSb} [\text{Cs}]$  where  $[\text{Cs}]$  indicates a surface treatment with Cs, the amount of Cs being unknown but small compared with that of the two other alkali metals. The present method of obtaining this complex material comprises the following steps:

- (1) As in the case of the  $\text{Cs}_3\text{Sb}$  cathode, antimony is evaporated to a predetermined light transmission of approximately 85%. For this measurement a 2870°K tungsten lamp is used as light source and a Weston illuminator meter model 756 as detector.
- (2) The Sb film is exposed to K at a temperature of approximately 160°C to form the compound  $\text{K}_3\text{Sb}$ , as indicated by a peak in photoemission. The photoemission is monitored throughout the process in the white light from a tungsten lamp (approx. 2870°K.)
- (3) This compound is exposed to Na vapor at a temperature of approximately 220°C. At this temperature,  $\text{K}_3\text{Sb}$  decomposes and the K is gradually replaced by Na. This process is continued until the decrease in photoemission indicates that the ratio of Na to K exceeds the value 2:1.
- (4) The compound  $\text{Na}_{\frac{1}{2}}\text{K}_{\frac{1}{2}}\text{Sb}$  is exposed at 160°C to alternating additions of K and Sb until a peak in photoemission indicates that the ratio Na:K = 2:1 is reached, corresponding to the formula  $\text{Na}_2\text{KSb}$ .
- (5) Finally, this two-alkali photocathode is exposed to Cs vapor at approximately 160°C to obtain the high red response typical of the three-alkali cathode. In some cases, further addition of Sb is also required to achieve peak sensitivity. The addition of Cs is discontinued when peak photoemission is reached.

From the above schedule, it is evident why the amount of Sb in the final cathode cannot be predetermined. Although the initial amount of evaporated Sb is reproducible, the additional amounts required during steps (4) and (5) vary from cathode to cathode, depending on the degree of deviation from the 2:1 ratio at the end of step (3).

From the details of the schedule, it is also apparent that the correct ratio of Na to K has to be obtained by a slow and cumbersome method very much in contrast to the simple and almost automatic way in which the right amount of Cs is incorporated into the  $\text{Cs}_3\text{Sb}$  cathode. This difficulty of adjusting the Na:K ratio is the major obstacle to fabricating

multi-alkali cathodes in quick succession or simultaneously as would be required for large scale production. An additional complication is the final Cs activation which, as pointed out above, may require further evaporation of Sb and, in general, is still the least understood phase of the process.

Another source of irreproducible photosensitivity which can be eliminated more easily in  $\text{Cs}_3\text{Sb}$  cathodes than in multi-alkali cathodes should be mentioned. It is customary to produce the alkali metals within the tube by a chemical reaction between an alkali metal salt and a reducing agent (see, for instance, Ref. 4). Even with thorough preliminary outgassing, it is unavoidable that during this chemical reaction some gas be released which may affect the sensitivity of the photocathode. In  $\text{Cs}_3\text{Sb}$  cathodes, this contamination can be avoided by releasing the Cs metal before the Sb film is deposited. In multi-alkali cathodes, the alkali metals are produced one by one in the course of the process; especially during the release of Cs in step (5) the presence of contaminating gas is often indicated by an initial drop in sensitivity, accompanied by a transient rise in pressure.

After the above description of the most serious problems associated with the multi-alkali process, it may be appropriate to formulate below some of the questions that may be answered by experimental studies of the kind reported in Sections II and III.

- (1) Is it possible to release all three alkali metals before the Sb deposition to avoid gas contamination?
- (2) Can an activation process be devised in which the "right" amount of Na and K is introduced without the need for later readjustment of the ratio?
- (3) How critical is the Na:K ratio? This is perhaps the most important question. To illustrate by an arbitrary example: If high sensitivity requires that the Na to K ratio of 2:1 be accurate within  $\pm 5\%$ , the chances are good that a procedure may be developed whereby predetermined amounts of Na and K are introduced. If - as may well be possible - a deviation from stoichiometry by 1% or even .1% is detrimental, it may be difficult to improve on the present method

involving steps (2), (3), and (4).

- (4) Is there an optimum amount of Cs and, if so, how great is it? (For example, does it correspond to one monatomic layer, to several monatomic layers, or to a fraction of one monatomic layer?)
- (5) If, as observations indicate, the optimum amount of Cs varies from cathode to cathode, what determines this optimum amount? Is there one particular step in the previous history of the cathode which is important?
- (6) What is the effect of superficial oxidation on the photoelectric properties?

These are the main questions considered in the following sections. However, the list is by no means complete and many other characteristics deserve further study; for instance, what determines the long wavelength threshold and can it be extended into the infrared? How is the photoelectric sensitivity related to the crystal structure? What is the effect of varying the temperature during one or more of the processing steps? What is the relationship between the photoelectric response and the dark resistance of the cathode material?

## II. ACTIVATION PROCESS EXPERIMENTS

### A. Tube Design

Since each activation experiment requires a separate tube, significant results can be obtained within a reasonable time only by using the simplest possible tube design. Therefore all the experiments described in this section were made with diodes of the type shown diagrammatically in Fig. 1. Sb is evaporated from a bead in the center of the spherical glass envelope onto approximately one-half of the bulb area. The thickness of the layer is monitored in the usual way by measuring the light transmission during the evaporation. Two Pt strips are sealed into the glass to make contact to the cathode and to permit resistance measurements across the cathode films. The central evaporator is used as the anode by maintaining it at about 100 volts above cathode potential.

Since very thin cathode films are often so resistive that photoemission measurements are difficult to make, a conducting substrate was provided in some tubes by evaporating tungsten from a helix made of 0.005" W wire and mounted close to the Sb bead in the center of the tube. It was found that in this way a sufficiently conducting substrate for the cathode could be produced with a light loss of only about 10%.

## **B. Attempts to Produce Clean Alkali Metals**

Two approaches were tried to eliminate the contamination of photocathodes by gas evolved during the release of alkali metals. The first consisted of modifying the method of producing the alkali metal in such a way that less or no gas is released during the chemical reaction. The second was to explore a procedure whereby all the gas is released before the cathode has reached the stage where it is readily contaminated. The results obtained are described below.

### **a. New Cesium Generators**

The conventional Cs generator consists of a narrow (about 1 mm diameter) nickel cylinder filled with a mixture of cesium chromate and silicon powder. With the object of obtaining a generator which may contain less gas and is less likely to be affected by water vapor, tests were made on generators composed of thin nickel strips carrying evaporated coatings of cesium chromate and aluminum, the latter to serve as the reducing agent. Contrary to expectation, these generators were quite gassy. In the next experiment, the generators were therefore baked in air prior to incorporation in the tube, but the gas release on flashing was still excessive. Further investigations would be required to find and eliminate the origin of this unexpected gas content.

### **b. Pre-flashing of Alkali Metal Generators**

To eliminate the effect of gas release during later stages of the process, three tubes of the type shown in Fig. 1 were made in which the channels were heated to the reaction temperature before the evaporation of Sb, so that small amounts of all three alkali metals were released. The tubes were then heated to 300°C to remove all the free alkali metal and activated by the

standard process. As a result of this preliminary treatment, the release of alkali metal during the later stages of the process was not accompanied by degassing and contamination of the surfaces; however, none of the tubes had the high final sensitivity of a typical multi-alkali cathode.

In case these results were due to alkali metal remaining in the tube after the bake, one tube was made in which it was attempted to remove the pre-flashed alkali metals by oxidation. After evaporation of Sb and the subsequent processing with Na and K, the cathode had high red response which could only be understood by assuming that metallic Cs was still present in the tube after oxidation. A possible explanation may be that the pre-released Cs reacted with the Sb bead and was thus not completely oxidized. During evaporation of the Sb, it may then have reappeared through the decomposition of the Cs-Sb compound.

Since the experiments just described indicated that more radical measures have to be taken to ensure complete elimination of free alkali metal after pre-flash, a tube was made in which the bake at 300°C was supplemented by heating of the Sb bead to remove, by decomposition, any alkali metal that might have reacted with the bead; moreover, oxygen was introduced into the tube after cooling to ensure that no alkali metal remain in the elementary form. Even so, the tubes showed abnormal features during the subsequent standard multi-alkali process: (1) red response was obtained immediately after the formation of  $K_3Sb$  whereas it usually only appears after addition of Na and Cs; (2) the cathode did not show the typical  $K_3Sb$  color (purplish in transmitted light); and (3) addition of Na and Cs did not increase the sensitivity in the usual way.

The most likely explanation seemed to be that despite all the precautions taken to remove free alkali metal,

enough Cs was retained, possibly in the glass walls, to interfere with the activation process and to cause the red response in an earlier stage. As a simple control experiment, a tube was therefore made in which only K and Na were preflashed and removed by baking and oxidizing as described above. With this tube, a completely standard activation process was successful so that one is forced to the conclusion that residual Cs was, in fact, present in the earlier experiments. The most interesting aspect of these results is that the activation process should be so unfavorably affected by the presence of minute amounts of Cs in the early stages.

The harmful effect of the residual alkali metal, together with the difficulties encountered in removing it, make it likely that the preflash method is not of immediate practical value, although it accomplishes the original objective of eliminating gas release during the process. Therefore this approach was not pursued, but it should be emphasized that the effect of residual traces of alkali metal on the cathode sensitivity is in itself an interesting and unexpected phenomenon which may deserve further study.

#### C. Effect of Oxygen on Multi-Alkali Cathodes

Earlier experiments (Ref. 3) have indicated that the multi-alkali cathode is the only photocathode of high quantum efficiency which does not benefit from superficial oxidation. Three experimental tubes were made to come to a final conclusion as to the effect of oxygen.

In the first tube, a normal multi-alkali cathode was gradually oxidized while the sensitivity to white light as well as to red and blue light (Corning filters 2408 and 5113) was monitored. The following readings were obtained.

	<u><math>\mu\text{a/l}</math></u>	<u>with red filter</u>	<u>with blue filter</u>
Before oxidation:	100	26	6.0
1st oxidation:	54	8	3.6
2nd oxidation:	4	1	0.6

There was no rise in the sensitivity at any time. It is interesting to see that on first exposure the red response appears to drop more than the blue response, indicating an increase in the surface barrier (electron affinity). This is surprising because it is directly opposite to the effect on the  $\text{Cs}_3\text{Sb}$  cathode (Ref. 2) and also on the  $\text{Ag-O-Cs}$  (Ref. 5) and the  $\text{Bi-Ag-O-Cs}$  (Ref. 6) cathodes where superficial oxidation causes an increase in red response and threshold wavelength which is usually attributed to a reduction in electron affinity.

In a second tube, the possibility was investigated that introduction of oxygen at an earlier stage in the activation process may be beneficial. Therefore the  $\text{Na}_2\text{KSb}$  cathode was exposed to oxygen before the introduction of Cs. Again, the sensitivity dropped at once and the red response, which was very low to begin with, disappeared completely. The final Cs activation produced normal three-alkali color response but low over-all sensitivity; in other words, the intermediate oxidation had definitely no beneficial and possibly a detrimental effect.

Finally, in a third tube a control experiment was made by superimposing a  $\text{Cs}_3\text{Sb}$  cathode onto a multi-alkali cathode and then exposing the surface to oxygen. To eliminate the effect of the increasing thickness of the cathode film on the sensitivity, all measurements were made with the light incident on the vacuum interface. The results are summarized below:

	<u><math>\mu\text{a/l}</math></u>	<u>with red filter</u>	<u>with blue filter</u>
$\text{Na}_2\text{K(Cs)Sb}$ cathode:	94	10	10
After addition of $\text{Cs}_3\text{Sb}$ :	32	3	4
1st oxidation:	34	?	?
2nd oxidation:	30	6	3
3rd oxidation:	11	1.6	1.2

These readings can be interpreted as follows: During the addition of  $\text{Cs}_3\text{Sb}$ , the cathode loses sensitivity in accordance with the general experience that  $\text{Cs}_3\text{Sb}$  cathodes are inferior to multi-alkali cathodes. The red response is still higher than that of a standard  $\text{Cs}_3\text{Sb}$  cathode for one or both of two reasons; either the  $\text{Cs}_3\text{Sb}$  cathode is not thick enough or a diffusion takes place so that the materials are intermingled near the surface. The effect of oxygen is typical for a  $\text{Cs}_3\text{Sb}$  cathode (though less pronounced) in that the total sensitivity drops after a slight initial increase while the red response continues to rise beyond the point where the blue response starts to decrease. This means that there was enough  $\text{Cs}_3\text{Sb}$  material in the surface to change the detrimental effect of oxygen on red response in the  $\text{Na}_2\text{K}(\text{Cs})\text{Sb}$  cathode to the beneficial effect typical for  $\text{Cs}_3\text{Sb}$ . It is worth mentioning that this finding explains a statement in an earlier Russian publication (Ref. 7) that oxidation of multi-alkali cathodes is only beneficial for low-sensitivity cathodes. One may assume that these cathodes had low sensitivity because they contained so much Cs that considerable amounts of  $\text{Cs}_3\text{Sb}$  were formed.

#### D. Activation Process with Predetermined Amounts of Antimony

As was pointed out in Section I, the amount of Sb in cathodes activated in accordance with the described schedule varies, dependent on the amount of K required (during step 4) to compensate for the excess Na. In addition, this replacement process is likely to cause some of the non-uniformity over the area of the cathode often found in multi-alkali cathodes. In principle, it should be possible to eliminate this inherent cause of irreproducibility by a process in which as a first step the compound  $\text{Na}_2\text{Sb}$  is produced. In a second step,  $\text{Na}_3\text{Sb}$  could then be converted into  $\text{Na}_2\text{KSb}$  by alternating addition of K and Sb. Thus a well defined thickness of Sb could be obtained by carrying out the Na reaction with two-thirds of the amount of Sb required in the final cathode.

A series of seven experimental diodes were processed to study the feasibility of this suggestion. One of the expected difficulties was the high resistivity of the initial layer because the amount of evaporated Sb has to be reduced to two-thirds of the amount used in the conventional process. For this reason, three of the diodes were provided with transparent tungsten substrates as described in II-A.

Sb layers of different thicknesses (corresponding to values of light transmission between 70% and 95%) were evaporated and then saturated with Na to form  $\text{Na}_3\text{Sb}$ . This was followed by alternately adding K and Sb to form  $\text{Na}_2\text{KSb}$  and by the final activation with Cs. The results led to the following conclusions. First, cathodes made by this process seemed to show the expected greater degree of uniformity. Second, the sensitivity of the  $\text{Na}_2\text{KSb}$  film was of the same order as that obtained by the standard activation process, i. e., in the range of 30 to 40  $\mu\text{a}/1$ . Third, the final step of adding Cs and Sb produced in all tubes much lower sensitivity than that obtained by the standard process, particularly at longer wavelengths. However, normal sensitivity could be obtained by repeating the whole activation cycle, that is, by introducing more Na and then compensating for the excess Na with K. If this re-processing should prove unavoidable, the advantages of the process are, of course, eliminated. At present there is no reasonable explanation as to why the effect of Cs on  $\text{Na}_2\text{KSb}$  cathodes of similar sensitivity should depend on the method by which the  $\text{Na}_2\text{KSb}$  compound has been made. An answer to this puzzle will probably have to await a better understanding of the mechanism by which the Cs reduces the surface barrier. Qualitatively, one may speculate that the particle size of the  $\text{Na}_2\text{KSb}$  crystals varies with the method by which they are formed and that the particle size affects the binding forces exerted on the Cs atoms.

#### E. Modification of the Cesium Process

Experiments were made to introduce Cs after the formation of  $\text{K}_3\text{Sb}$  and before the formation of  $\text{Na}_2\text{KSb}$ . The main purpose of these experiments was to gain a better understanding of the Cs activation, but it was also expected that the earlier use of Cs would reduce the detrimental effect of released gas which seems to be more harmful if it occurs in the final stages of the process.

A total of five diodes were processed with early introduction of Cs. In all cases the introduction of Cs was stopped when the photoemission had reached a peak. The results are summarized below.

- (1) No difficulty was experienced in obtaining sensitivities in the range of 150  $\mu\text{a}/1$ ; compared with the standard process, the cathodes seemed to be more uniform (possibly due to the reduced gas contamination) and to have a higher blue-to-red ratio in spectral response. On the other hand, none of the cathodes reached the 200  $\mu\text{a}/1$  range which is frequently obtained with standard multi-alkali cathodes. All these differences are marginal and, considering the small number of

tubes, may not be significant. The essential point is that typical multi-alkali sensitivity can be obtained by this process.

- (2) A single exposure of  $K_3Sb$  to Cs was sufficient to produce multi-alkali response in the final cathode. Alternating the addition of Cs and Sb, as is often required in step (5) of the standard process, did not cause either an increase or a decrease in sensitivity; however, a final Cs treatment after the formation of  $Na_2KSb$  proved actually detrimental. These findings were quite unexpected. It is usually assumed that the role of the Cs is to form a surface film which lowers the barrier for the escaping electrons. If this assumption is correct, the experiments would indicate that after the addition of Na, K, and Sb, the "right" amount of Cs diffuses to the surface even though the total amount of Cs in the cathode may vary. Moreover, it seems likely that the amount of Cs bound by  $K_3Sb$  is smaller than that introduced during the standard process in step (5); this makes the profound effect on the final sensitivity even more surprising. Finally, the successful introduction of Cs in the earlier stage is in strange contrast to the detrimental effect of Cs in the pre-flash experiments reported in II-B. All the experimental results emphasize again how much has still to be learned about the nature of the Cs activation.
- (3) In one tube, the possibility was explored that in this modified process without final Cs activation, superficial oxidation may be beneficial, although it has proved invariably detrimental in standard three-alkali cathodes (see II-C). The effect of oxygen turned out to be the same as on standard cathodes, i. e., the red response dropped at once sharply.

### III. MOLECULAR BEAM EXPERIMENTS

#### A. Introduction

On the basis of past work on the alkali antimonides in general and the

multi-alkali cathode in particular, it seems to be established that the cathode consists essentially of the stoichiometric compound  $\text{Na}_2\text{KSb}$  whose electron affinity has been reduced by a surface layer containing Cs. The sensitivity values obtained prior to the Cs treatment are reasonably consistent, indicating that the present process of obtaining the correct ratio of Na:K (2:1), though cumbersome, is satisfactory at least to within the required limits.

By contrast, it is evident both from the experiments reported in Section II and from general experience that our understanding of the role of Cs and hence of the optimum Cs activation is still very unsatisfactory. As a result, the final sensitivity values of three-alkali cathodes still show a wide spread; while sensitivities as high as  $250 \mu\text{a}/1$  are occasionally obtained, it is not uncommon to find cathodes which barely reach  $100 \mu\text{a}/1$  under apparently similar processing conditions. It seems that two specific questions require an answer before consistent progress in the manufacture of cathodes can be expected. First, the absolute amount of Cs required for optimum sensitivity should be established as well as approximate limits within which this value can be varied without seriously affecting the sensitivity. Second, it would be desirable to find out in which form the Cs is bound in the material; among the many possibilities, a few may be mentioned: The Cs may be present in the form of a monomolecular layer of  $\text{Cs}_3\text{Sb}$  or of small  $\text{Cs}_3\text{Sb}$  particles dispersed in the  $\text{Na}_2\text{KSb}$  compound; it may also form new compounds in the surface such as  $\text{NaKCsSb}$  or other combinations of the three alkali metals with Sb. The spread in sensitivity values may be due to changes in the absolute amount of Cs and/or in the form in which it is incorporated.

The absolute amounts of Na and K in the cathode have been established with reasonable accuracy by chemical analysis (flame spectrophotometry) and with greater accuracy by X-ray studies (Ref. 8). These methods are satisfactory for the amounts involved (between 10 and 1,000  $\mu\text{g}$ ) but not for the much smaller amounts of Cs contained in the cathodes. The X-ray method is not sensitive enough and the chemical method is excluded because it cannot distinguish the Cs in the cathode film from Cs bound by the glass or other parts of the tube which may represent much larger amounts. The use of radioactive Cs was considered, but apart from the large amount of time required to perfect the technology for this approach, it may again give false answers because of the Cs atoms bound by tube parts. It was finally decided that the most promising method for a quantitative determination of Cs would be the use of the atomic beam method.

The basic idea of this technique, as applied to the problem of Cs activation, is as follows: An evaporated layer of Sb of accurately known thickness (expressed in atoms per  $\text{cm}^2$ ) is processed in the conventional way to produce a  $\text{Na}_2\text{KSb}$  photocathode. This cathode is then exposed to a beam of Cs atoms of accurately controlled intensity; by suitable choice of the parameters, it is possible to reduce the number of Cs atoms incident on the cathode to extremely small values. For instance, the number corresponding to a monatomic layer can be deposited over a period of minutes. Quantities of this order of magnitude could hardly be determined accurately by any other method.

The method of using calibrated Cs-beams for surface treatment in electron emission studies was developed at RCA laboratories by R. E. Simon (Ref. 9). The availability of the technique and the necessary equipment stimulated the decision to use beam techniques for photocathode problems. Originally, it was planned to use the beam method in three successive steps as follows:

- (1) The beam calibration was to be checked by activating an Sb film of known thickness with a Cs beam to form  $\text{Cs}_3\text{Sb}$ . Since the composition of this material is well established, the required amount of Cs is known in advance and should agree with the amount calculated from the beam parameters.
- (2) The beam should then be used to add Cs to an activated  $\text{Na}_2\text{KSb}$  cathode to determine the optimum Cs content of the three-alkali cathode under different conditions.
- (3) If the method proved successful with Cs, it was also planned to apply it to Na and K to find an answer to a question raised in Section I, i.e., to what degree small deviations from the Na:K ratio of 2:1 affect the photo-sensitivity.

As will be seen below, many unexpected difficulties slowed down the progress with the beam experiments so that only the first two problems could be tackled. The results are still of a preliminary nature; on the other hand, they have produced some interesting new information which is of general interest. In subsection B, the experimental arrangements and the calculations required for beam calibration will be described. The results of the experiments will be reported in subsection C.

## B. The Cesium Beam Technique

### a. General Considerations Concerning Atomic Beams

According to the kinetic theory of gases, (Ref. 10) in a closed chamber under equilibrium conditions, the number of atoms striking a unit area can be calculated from the formula

$$N = 5.83 \cdot 10^{-2} \cdot \frac{pA}{(MT)^{1/2}} \text{ atoms/cm}^2/\text{second} \quad (1)$$

In this equation,  $p$  = vapor pressure of the material at temperature  $T$  in mm Hg

$A$  = Avogadro's number =  $6 \cdot 10^{23}$

$M$  = atomic weight

$T$  = temperature of the material in  $^{\circ}\text{K}$

If the chamber is provided with an aperture of area  $a$ , which is small enough so that the equilibrium in the chamber is not appreciably changed, those atoms which normally strike area  $a$  will be emitted. An atomic beam can be formed by interposing a defining aperture to intercept all atoms except those directed toward the substrate. All atoms are intercepted except those in a small cone, the axis of which lies on the line perpendicular to and passing through the center of the small aperture. Since it has been shown that for a thin aperture as used here, the atoms are emitted from the small aperture in a cosine distribution, the beam intensity at a point  $r$  cms distant from the small aperture can be calculated from the formula (Ref. 11)

$$N = 5.83 \cdot 10^{-2} \cdot \frac{pA}{(MT)^{1/2}} \cdot \frac{a}{\pi r^2} \text{ atoms/cm}^2/\text{second} \quad (2)$$

It should be emphasized that Eq. (2) gives a value for the number of atoms incident on the substrate; it obviously gives no information as to the number of atoms which are permanently adsorbed.

With a tube of given design, all the parameters are constant except for  $T$  and therefore  $p$ . The vapor pressure  $p$  can be calculated (Ref. 12) from the equation

$$\log p = 11.0531 - 1.35 \log T - \frac{4041}{T} \quad (3)$$

or - more conveniently - it can be derived from published curves. (Ref. 13)

In the case of Cs, the value for N calculated from Eq. (2) can be checked by two methods. The first (Ref. 14) depends on the fact that if a tungsten filament exposed to the Cs beam is hotter than 1200°K, all Cs atoms incident on the filament are evaporated as positive ions which can be collected by an electrode held at a negative potential relative to the filament. The collected current will be

$$I = N \cdot e \cdot f \text{ amps} \quad (4)$$

In this equation,  $N$  = number of atoms/cm<sup>2</sup>/second (as in Eq. 1)  
 $e$  = electronic charge =  $1.6 \cdot 10^{-19}$   
 $f$  = area of filament exposed to beam in cm<sup>2</sup>

The second method of checking the value of N obtained from Eq. (2) is based on the observation (Ref. 15) that the work function of tungsten as a function of Cs coverage is lowest, and hence its photoemission highest, when the surface contains one Cs atom for every four W atoms. Assuming  $10^{15}$  W atoms per cm<sup>2</sup>, one obtains the equation

$$N = \frac{10^{15}}{4} \cdot \frac{1}{t} \quad (5)$$

where  $t$  is the time (inseconds) required for the photoemission to reach a maximum.

Some comments may be in order concerning the sources of error in measuring the parameters used in Eqs. 1, 2, 4, and 5. The main problem in the use of all four equations is probably the accurate determination of the temperature of the Cs reservoir and the need to keep this temperature constant within narrow limits. When Eq. (4) is used, experimental difficulties may also arise in measuring the area of the tungsten filament accurately. An uncertainty in Eq. (5) resides in the assumption that the surface contains  $10^{15}$  W atoms per cm<sup>2</sup>. It is known that this number varies with the crystal face of the tungsten surface and is therefore not known in most practical cases.

For easier reference, this may be an appropriate place to record some equations used for the conversion of various parameters which occur frequently in connection with thin film deposition.

If a bead of weight  $w$  (in milligrams) is evaporated from a distance  $r$  (in cm), the weight  $u$  deposited per unit area, assuming uniform evaporation over the sphere with radius  $r$ , is

$$u = \frac{w}{4\pi r^2} \cdot 10^3 \text{ microgram } (\mu\text{g}) / \text{cm}^2 \quad (6)$$

If the density  $s$  of the deposited material is assumed to be the same as that of the bulk material, the thickness  $T$  of the deposit is

$$T = \frac{u}{s} \cdot 10^{-6} \text{ cm} = \frac{u}{s} \cdot 10^2 \text{ angstroms} \quad (7)$$

or

$$T = \frac{w}{4\pi r^2 s} \cdot 10^5 \text{ angstroms} \quad (7a)$$

The number  $n$  of atoms deposited per unit area is

$$n = u \cdot A \cdot \frac{1}{M} \cdot 10^{-6} \quad (8)$$

where  $A$  is Avogadro's number  $= 6 \cdot 10^{23}$  and  $M$  is the atomic weight.

The thickness of a monatomic film  $t_m$  can be calculated from

$$t_m = \sqrt[3]{\frac{M}{sA}} \text{ cm} = \sqrt[3]{\frac{M}{s} \cdot 1.6 \cdot 10^{-24}} \text{ cm} = \sqrt[3]{1.6 \cdot \frac{M}{s}} \text{ angstroms} \quad (9)$$

#### b. Tube Designs for Cs Beam Experiments

The final design of the tube used for the beam experiments is shown diagrammatically in Fig. 2. A known amount of Sb is evaporated from a retractable evaporator onto the flat window of the tube which is provided with a cathode contact. During this operation, the shutter in front of the defining apertures is closed. Throughout the experiment, the one-inch diameter section of the tube is cooled with liquid nitrogen to make sure that Cs can reach the window only in the form of an atomic beam originating from the Cs reservoir and controlled by the temperature of this reservoir and the size of the gun aperture.

In all tubes, the values for the geometric parameters of Eq. (2) were approximately the same, viz., the aperture had a diameter of 0.06 cm and the distance from the aperture to the window was 19 to 20 cm. By using these values, together with the numerical values of  $a$  and  $M$ , one can plot  $N$  as a function of  $T$  as shown in Fig. 3.

## C. Experimental Results

### a. Introductory Remarks

A total of ten beam tubes were made which have been described in detail in the quarterly reports under this Contract. Since the early results were often confusing and contradictory, it is proposed to deal below separately with the different aspects of the experiments rather than with the individual tubes in chronological sequence. The results will be reported under the following subheadings: calibration of Cs beam with tungsten filament; problems of antimony evaporation; processing of  $\text{Cs}_3\text{Sb}$  cathodes with Cs beam; processing of  $\text{Na}_2\text{KSb}$  cathodes with Cs beam; and processing of  $\text{Cs}_3\text{Sb}$  cathodes in an enclosed chamber without any apertures.

### b. Calibration of Cs Beam

The calibration of the Cs beam by the two methods described under III-A was performed in several tubes. In the early tubes, considerable discrepancies were found but it is believed that these were mainly attributable to inaccuracies in measuring the temperature of the Cs reservoir and to temperature fluctuations. The required accuracy of temperature determination and constancy is quite formidable because the steep rise of vapor pressure with temperature has the effect that  $N$  increases almost twofold for a ten degree rise in temperature (see Fig. 3).

In later tubes, the values of  $N$  obtained from calibration with the W filament agreed within  $\pm 40\%$  with those calculated from Eq. (2). The agreement could probably be improved considerably by further refinement of the temperature measurement; in particular, there is some doubt as to whether the temperature measured with a thermocouple attached to the glass wall of the Cs reservoir is exactly the same as that of the Cs itself. At the present stage, no further improvement in calibration was attempted because the discrepancies found in the cathode experiments, to be described below, were of a much larger order. It must also be remembered that where quantities corresponding to one atomic layer or less are concerned, even with an error of  $\pm 40\%$ , better results may be obtained than by other methods.

### c. Problems of Sb Evaporation

In all the experiments where activation with a Cs beam is used, quantitative data can be obtained only if the quantity of the Sb on the substrate is accurately known. In the past, two methods have been used to accomplish this. In the first, a weighed amount of Sb is evaporated from a known distance so that the thickness can be calculated from Eq. (6), (7), or (8), according to whether the thickness is wanted in  $\mu\text{g}/\text{cm}^2$ , in angstroms, or in number of atoms per  $\text{cm}^2$ . This method was applied in some of the tubes, but it suffers from the inherent uncertainty that the Sb may not evaporate uniformly in all directions.

In the second method, Sb is evaporated until the light transmission through the deposited film is reduced by a predetermined amount. From earlier work, (Ref. 1) curves are available which relate the light transmission to the thickness of the film. Since these curves appeared well established, they were used for most of the tubes described below. However, the very large discrepancies obtained in the beam experiments aroused the suspicion that the above mentioned curves may not be correct, and it was therefore decided to remeasure the relation between thickness and light transmission.

The curves of Ref. (1) were obtained by evaporating a weighed amount of Sb onto a flat glass plate so that a wedge-shaped deposit was formed whose thickness could be determined from the distance of the source. If a large number of such measurements is made, the mentioned uncertainty regarding uniformity of evaporation can be overcome by taking the statistical mean. Earlier experiments of this nature at RCA laboratories had given very inconsistent results and it was suspected that the light transmission may be a function not only of the distance of the source but also of the angle under which the Sb atoms strike the substrate. Therefore an experimental tube was designed in which the light transmission could be measured for different amounts of Sb evaporated under similar conditions as in the beam tubes, i. e., from the same distance and with normal incidence. The transmission was measured with a  $2870^\circ\text{K}$  tungsten lamp as light source and a Weston Illumination Meter Model 756 as detector.

The tube is shown in Fig. 4. In a typical example, four beads of Sb weighing 4.1 mg each were mounted 12.8 cm from the glass window. Four circular areas of 1" diameter were marked out on the window, three of which were provided with a magnetically operated shutter. The light transmission in the open area was then measured during

evaporation of the first bead during which the three shutters were closed. Next, one shutter was opened and the second bead was evaporated. The light transmission could then be measured in two areas, one of which having now an Sb deposit twice the thickness of the other. In the same way, the third and fourth beads were evaporated, each time with an additional shutter opened. Thus with one tube ten different readings could be taken (four with the first area, three with the second, etc.) . From two tubes of this type sufficient points were obtained to draw a curve of light transmission vs thickness. This is shown in Fig. 5, together with the curve of ref. (1). It is apparent that for a given light transmission, the thickness values may differ almost by a factor of two. The deviation is in the direction that was expected from the cathode experiments discussed below.

#### d. Processing of Cs<sub>3</sub>Sb Cathodes with Cs Beam

As was mentioned under III-A, in the first experiments with the beam tube (Fig. 2), attempts were made to produce Cs<sub>3</sub>Sb cathodes to check whether the amount of Cs required to activate the photocathode agreed with that expected from the thickness of the Sb film, i. e. , whether the number of Cs atoms deposited per cm<sup>2</sup> during the activation (as derived from Eq. 2) is three times the number of Sb atoms per cm<sup>2</sup>. Before the experiments were begun, it had been anticipated that the greatest problem in the beam method would be that of the "sticking" factor. If an appreciable fraction of the incident Cs atoms does not adhere to the Sb film, absolute numbers for the amount of Cs incorporated into the cathode cannot be obtained by the beam method. A sticking factor below unity would manifest itself in the present experiment by an apparent Cs:Sb ratio in excess of the expected 3:1 value. An encouraging result of the first, and all subsequent, experiments was that a ratio greater than 3:1 was never obtained.

The first tubes were activated as follows ( in this report, the essentials will be emphasized; for more details see Quarterly Reports Nos. 2 and 3, Contract AF33(616)-8303): An Sb film was evaporated until the light transmission dropped to 60%, corresponding (Ref. 1) to - as was believed at the time - approximately 9 µg/cm<sup>2</sup>. The temperature of the reservoir was then adjusted to produce Cs<sub>3</sub>Sb within a period of a few hours and the shutter was opened. To ensure immediate reaction of the Cs with the Sb film, the window was held at a temperature of 140°C which is commonly used in the fabrication of Cs<sub>3</sub>Sb photocathodes. The experiment was successful only to the limited extent that a color change of the Sb layer was observed over a well-defined central area

of about 1" diameter, indicating that a Cs beam had indeed been produced. However, the photocurrent tended to drop at a stage where both color and photosensitivity indicated that only a fraction of the Cs required to form  $\text{Cs}_3\text{Sb}$  had arrived at the window. At this point, the heating of the window was discontinued and the cathode was cooled to room temperature. Quite unexpectedly, on re-starting the beam, the formation of  $\text{Cs}_3\text{Sb}$  proceeded quite normally and a  $\text{Cs}_3\text{Sb}$  cathode of the familiar reddish color and of above average sensitivity was obtained. Thus it appears that, on exposure to a low intensity beam of Cs, the rate of re-evaporation of Cs after an initial period (possibly corresponding to the stoichiometric compound  $\text{CsSb}$ ) exceeds the rate at which diffusion into the material and reaction with Sb occur. During the normal cathode fabrication, the Sb film is always exposed to a large excess of Cs which may explain why the reaction proceeds to completion even at the higher temperature.

The activation at room temperature was successfully repeated in subsequent tubes, but in all experiments the amount of Cs required for activation, as calculated from Eq. (2) and from tungsten filament calibration, was at least two and up to four times smaller than expected for the formula  $\text{Cs}_3\text{Sb}$ . For a long time this result was very puzzling until the measurements on the light transmission of Sb (see III-C-c) indicated that the Sb films in the beam experiments had been almost a factor of two thinner than assumed. If this correction is made, the results come much closer to the expected values, and it is possible that the remaining discrepancies could be reduced or eliminated by better temperature control.

Despite the great percentage errors in the beam experiments, the possibility of working with amounts corresponding to less than a monolayer has produced two interesting and useful results which are briefly summarized below.

- (1) When the cathode is exposed to the Cs beam beyond the point of maximum photosensitivity, the sensitivity decreases only very slowly. This can probably be attributed to a rapidly decreasing sticking factor after the formation of  $\text{Cs}_3\text{Sb}$  is completed. It is, of course, quite reasonable to expect at this stage a decrease in the forces which bind the Cs.
- (2) With the beam on, the peak sensitivity obtained is several times smaller than that of conventional  $\text{Cs}_3\text{Sb}$  cathodes. However, when the beam is turned off, the sensitivity increases about a factor of two and an additional increase of the same order is observed on brief heating of the cathode

to 130°C. After this treatment, the cathode has standard sensitivity. From this one must conclude that, with the beam on, the cathode contains more Cs than is needed for maximum sensitivity. Possibly the beam produces a compound of the exact composition  $\text{Cs}_3\text{Sb}$  whereas the material of highest sensitivity is known (Ref. 16) to contain a slight stoichiometric excess of Sb. Moreover, a slight excess of Cs on the surface may be unavoidable as long as the beam is on.

Some quantitative information concerning the amount of excess Cs introduced by the beam was obtained from one tube (#S. 1176). In this tube the beam intensity was approximately  $10^{13}$  atoms of Cs/cm<sup>2</sup>/sec. After peak sensitivity had been obtained by heating the cathode with the beam off, exposure to the beam for only 20 seconds sufficed to reduce the sensitivity by a factor of two. Hence about  $2 \cdot 10^{14}$  atoms per cm<sup>2</sup>, or less than a monatomic layer, had such a great effect on sensitivity.

#### e. Second Type Cs Beam Tube

A second type of Cs beam tube (Fig. 7) was also used in attempts to produce  $\text{Cs}_3\text{Sb}$  cathodes to check whether the amount of Cs required to activate the photocathode agreed with that expected from the original amount of Sb. This design was made with the thought that ultimately three reservoir - ovens could be placed in one tube allowing one to make a complete multialkali photocathode by beam techniques and perhaps a photocathode with known composition gradients across its area.

An initial tube without the shutter or liquid air trap was made to prove the design of the Cs reservoir - oven which was then modified to increase its radiation and reduce its mass in order to avoid an excessively long time constant for cooling. Two tubes of the design shown in Fig. 7 were tested. In one of these the reservoir - oven could not be brought to the proper temperature distribution, i.e., the aperture was the coldest part of the reservoir so that liquid Cs crept around the lip of the aperture and evaporated much faster than predicted. The other ran satisfactorily and gave a peak photosensitivity at  $2 \times 10^{16}$  Cs atoms per cm<sup>2</sup>. Chemical analysis (colorimetric) of the photocathode residue when the tube was opened gave 1.8 mg/cm<sup>2</sup> or  $.85 \times 10^{16}$  Sb atoms per cm<sup>2</sup> in reasonably close agreement with the formula  $\text{Cs}_3\text{Sb}$ . (However, the transmission monitoring of the Sb deposition was 60% to white light, which according to Fig. 5 would indicate three times this much Sb, but the light was incident at about 45° rather than normal.)

#### f. Processing of $\text{Na}_2\text{KSb}$ Cathodes with Cs Beam

Although the experiments with  $\text{Cs}_3\text{Sb}$  cathodes indicated that the method requires improvement before valid quantitative data can be obtained, two preliminary beam tubes were made with multi-alkali cathodes to gain some qualitative information as to the applicability of the method to this type of cathode. As a first step,  $\text{Na}_2\text{KSb}$  cathodes were produced on the window by the conventional process and sensitivities in the normal range were obtained (20 and 45  $\mu\text{a}/1$ , respectively.)

In the first tube (#S.1189), the sensitivity dropped at once when the shutter was opened to admit the Cs beam. However, it was found that the expected increase in sensitivity could be obtained by heating the cathode. This came as a surprise because just the opposite effect had been observed with the  $\text{Cs}_3\text{Sb}$  cathode, viz., the reaction proceeded better at room temperature.

In the second tube (#S.1213), the cathode was heated to about  $130^\circ\text{C}$  during exposure to the Cs beam. The intensity of the beam, as derived from Eq. (2), was approximately  $10^{11}$  atoms/ $\text{cm}^2/\text{sec}$ . and peak sensitivity was reached after 53 minutes, corresponding to approximately  $3 \cdot 10^{14}$  Cs atoms per  $\text{cm}^2$ . By alternating addition of Sb and Cs, a higher peak of 140  $\mu\text{a}/1$  was reached after a total Cs beam exposure of 165 minutes, corresponding to approximately  $10^{15}$  Cs atoms per  $\text{cm}^2$ .

Two comments may be made on this result: First, it shows the capabilities of the method; since the deposition of monolayer can be spread over several hours, the potential accuracy of controlling the amount of Cs is obviously enormous. Second, even if the results were quite accurate, it would still be impossible to express them in terms of monolayers because it is not known how many atoms of Cs per  $\text{cm}^2$  represent a monatomic layer on top of the complex cathode material. In other words, additional information, for instance from electron diffraction, is required to make a meaningful statement in terms of monolayers rather than of atoms per  $\text{cm}^2$ . Initial experiments with electron diffraction are reported under IV-D.

#### g. Processing of $\text{Cs}_3\text{Sb}$ cathodes in an Enclosed Chamber

On account of the unexplained discrepancies between calculation and experiment in the Cs beam tubes, a modified experiment based on similar principles was designed as follows. A Cs reservoir was produced at the bottom of a cylindrical tube, as shown diagrammatically in Fig. 6, by

distilling Cs from the side tube, indicated in the figure, while the lower part of the tube was cooled with liquid air. Sb was then evaporated from a removable evaporator onto the window of the tube until the light transmission was reduced to 60%. The tube was sealed off the pump system, and the temperature of the Cs reservoir was raised to a predetermined value. The number of Cs atoms striking the Sb film per  $\text{cm}^2$  per second can then be calculated for a given temperature with the aid of Eq. (1). Two tubes were processed by this method, one with the Cs at room temperature and the other with the Cs at  $-16^\circ\text{C}$ , corresponding to calculated activation times for  $\text{Cs}_3\text{Sb}$  of approximately 17 minutes and 21 hours, respectively.

The measured times agreed fairly closely with the calculated values, but subsequent experiments indicate that the good agreement must have been coincidental. First, the agreement was observed before the necessary corrections for the relationship between light transmission and thickness of the Sb film had been discovered. Second, control experiments were made to check the results by calibration with the tungsten filament, using the method of measuring the time required for obtaining peak photoemission from the filament. Whereas in the beam tubes these measurements were always reproducible in themselves despite the deviations from the values derived from Eq. (2), the times measured in the tubes of the type shown in Fig. 6 increased or decreased with each run. These changes appear to have two causes: (1) When Cs is first released from the reservoir, adsorption of Cs on the wall prevents an equilibrium pressure of Cs being established, i. e., the number of Cs atoms reaching the W filament is smaller than that calculated from the temperature of the reservoir. (2) If the glass wall has been exposed to Cs for a long time, the measured times are much shorter than calculated, apparently as a result of Cs being transferred from the glass to the filament in addition to the Cs evaporating from the reservoir.

It appears from these results that the Cs beam technique, despite its present shortcomings, is the more promising approach if quantitative information is required involving extremely small amounts of Cs atoms.

#### IV. MISCELLANEOUS EXPERIMENTS AND NOTES

##### On Evaporated Alkali Metal Generators

Except for the excessive gas evolution the new Cs generators (mentioned in II-B-a page 8) were satisfactory. The evaporation of cesium chromate

proceeded smoothly and completely from a platinum boat when the original chromate (as fine crystals) was pressed into tablets (3/16" dia and about .10" thick) before loading into the platinum boat. The nickel strips used were .10" wide and .0005" thick. They were coated on one side by evaporation of 400 mg of cesium chromate from the platinum boat at 5 1/2" throw, followed by an evaporation of 1200 mg of Al from tungsten coils at 4 1/2" throw. The demountable system (oil pumped and liquid nitrogen trapped) was let down to air, the strips turned over and the process repeated on the other side. Five of these strips were bound into a channel of more .0005" nickel to form the final generators. If thinner nickel strips, such as .0002", had been available they would have been used to reduce the current required to release Cs from these generators.

It is quite possible that potassium generators can be made in this same way by evaporating the chromate, followed by a reducing agent on inert metal strips. Sodium generators of this type may not be quite so easily made because the chromate did not appear to evaporate readily. It was found possible to fuse powdered chromate on the nickel strip, instead of evaporating it on, as an alternative method of application.

These evaporated alkali metal generators should be quite resistant to burn-out because the thermal conductivity of the nickel strips and the uniformity of the coatings should prevent hot spots which lead to burn-out.

#### B. Vapor Pressure Considerations

In most photocathode processing, cesium is released into the tube where it reacts with and is bound by the remainder of the photocathode material; any excess is ultimately pumped out since the tube is continuously being pumped. This system does not perform the activation under clear-cut conditions. The cesium beam experiments are intended to allow a definite amount of cesium to fall on the photocathode.

The opposite extreme would be to expose the photocathode to a definite pressure of Cs vapor, i. e., not to pump the tube during cesiation. This appears to be an attractive method for practical phototubes, but was found to suffer from difficulties in attaining the equilibrium pressure within the tube as described in III - C - f page 23.

An experimental tube very similar to that shown in Fig. 6 was made in order to try to define the regions of temperature and Cs vapor pressure in which  $\text{Cs}_3\text{Sb}$  and  $\text{CsSb}$  are found, cycling temperature or pressure back and forth between a  $\text{Cs}_3\text{Sb}$  film and an Sb film. Unfortunately the cycling broke up the film, preventing proper detection as to which compound was present. A diagram of the type shown in Fig. 8 was expected.

Had this experiment defined the regions of stability of  $\text{Cs}_3\text{Sb}$ , then further work on the more elaborate problem of the regions of stability of  $\text{Na}_2\text{KSb}$  as a function of Na and K vapor pressures might have been in order, leading to diagrams of the type shown in Fig. 9.

### C. Monitoring Problem

During the formation of the photocathode it would be desirable to have more information about the particular state than that given by the usual photosensitivity measurement. This is especially true for the multi alkali where it would be very useful to know in what direction the composition deviates from that desired. Consideration was given to the use of ellipsometry (study of the phase and amplitude changes suffered by light reflected from the layer when incident at an angle to the normal) which is capable of giving considerable information about such layers. It appeared that this approach would require considerable study and experimentation. This was not pursued because it was felt that other work which would lead to a better understanding of the photocathode processing is more important at the present time.

### D. Electron Diffraction

In order to obtain information about the photocathode layers which would lead to better understanding, it would be desirable to obtain electron diffraction patterns which could be watched during the processing. One tube was made to obtain an electron diffraction pattern from a completed  $\text{CsSb}$  surface. Unfortunately this had a leak and allowed only one test in which a 300 volt electron beam was used. This was scattered diffusely and no structure was observed in the scattered pattern. The beam was formed by two pinholes .002 and .004" diameter, 1.2" apart. The detection end of the tube was an image orthicon gun and target system.

## V. SUMMARY AND CONCLUSIONS

Work under this Contract had essentially two aims, i. e., improvements of the activation process of multi-alkali (S-20) photocathodes and a better understanding of the emission mechanism of this type of cathode.

The results of the processing experiments may be summarized as follows:

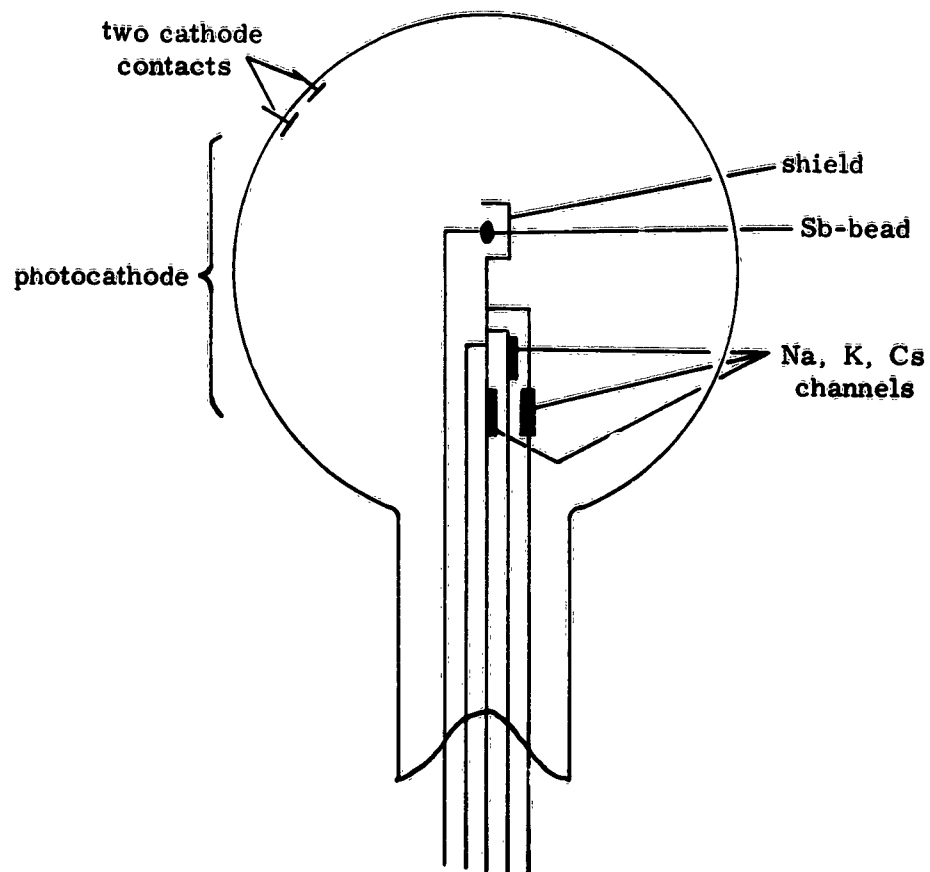
- (1) Attempts were made to eliminate the detrimental effect of the gas set free during the release of the alkali metal. It was found that pre-flashing of the alkali metal generators was effective in preventing gas release during the activation process but had a detrimental effect on the final sensitivity, particularly in the case of cesium. In an alternative approach, a new type of generator was studied, consisting of nickel strips coated with evaporated cesium chromate and aluminum as the reducing agent. So far, these new generators have not shown the expected absence of gas release.
- (2) Experiments to improve the sensitivity by introducing small amounts of oxygen confirmed that oxygen is detrimental to S-20 cathodes, irrespective of the stage in the processing where it is introduced. This is in sharp contrast to all the other photocathodes of high response to visible light (S-1, S-11, S-10), in which superficial oxidation causes an improvement, particularly in red response. In S-20 cathodes, superficial oxidation in all cases produced an immediate drop in red response.
- (3) Attempts were made to simplify the activation process and at the same time to obtain cathodes of greater uniformity and reproducibility by converting  $\text{Na}_3\text{KSb}$ , rather than using the conventional sequence of starting with  $\text{K}_3\text{Sb}$  with subsequent addition of Na and K to obtain the required ratio of the alkali metals. With the modified process, two-alkali cathodes of the usual sensitivity and enhanced uniformity were, in fact, obtained; however, the final activation with Cs did not lead to the high sensitivity of conventional S-20 cathodes. This effect of the previous history on the Cs activation was quite unexpected and is still unexplained.
- (4) Introduction of Cs before the introduction of Na produced typical S-20 response with only one exposure to Cs at this early stage in the process. This result was quite unexpected because it is usually assumed that Cs affects mainly the surface barrier of the material. Additional

exposure of cathodes made by this process to Cs vapor actually reduced the sensitivity.

The basic idea underlying the molecular beam experiments was the belief that the beam technique represents the simplest method by which the very small amounts of alkali metal involved in cathode activation can be accurately determined. By suitable choice of temperature and geometry, amounts corresponding to only a monolayer of alkali metal can be deposited over a period of minutes or even hours. The main problems to be answered by the beam method were, first, to find the absolute amount of Cs required for optimum sensitivity and, second, to establish the deviation from the 2:1 ratio of Na to K in the S-20 cathode within which high sensitivity can be obtained.

Progress of this work was greatly delayed by difficulties encountered in preliminary calibration experiments with  $\text{Cs}_3\text{Sb}$  cathodes. Using published values for the relationship between thickness and light transmission of evaporated antimony films, the amounts of Cs, as calculated from the beam parameters, were much smaller than had been expected from the formula  $\text{Cs}_3\text{Sb}$ . After many attempts to establish the cause of this discrepancy, it was finally attributed to errors in the determination of the amount of Sb in the cathode film. Separate experiments indicated that the relationship between thickness and light transmission of Sb films differs from the published values by a factor of two. The delay caused by this investigation prevented a completion of the beam experiments, but the following preliminary results are worth mentioning:

- (1) Cs reacts instantaneously with a thin Sb film maintained at room temperature until the composition  $\text{Cs}_3\text{Sb}$  is reached, i. e., the "sticking factor" is unity. As soon as the 3:1 ratio is reached, the sticking factor decreases rapidly, in agreement with expectation.
- (2) Peak sensitivity corresponds to a slight excess of Sb over the ratio 1:3 in agreement with previous findings that sensitive  $\text{Cs}_3\text{Sb}$  cathodes are p-type due to excess Sb.
- (3) Excess amounts of Cs corresponding to less than a monolayer reduce the sensitivity by 50%.
- (4) On exposure of the two-alkali cathode  $\text{Na}_2\text{KSb}$  to a Cs beam, S-20 response is only obtained if the cathode is heated to about  $130^\circ\text{C}$  during this process. The total amount of Cs needed for peak sensitivity appears to be of the order of a monolayer.



**Fig. 1 Experimental Tube for the Study of Photocathode Activation**

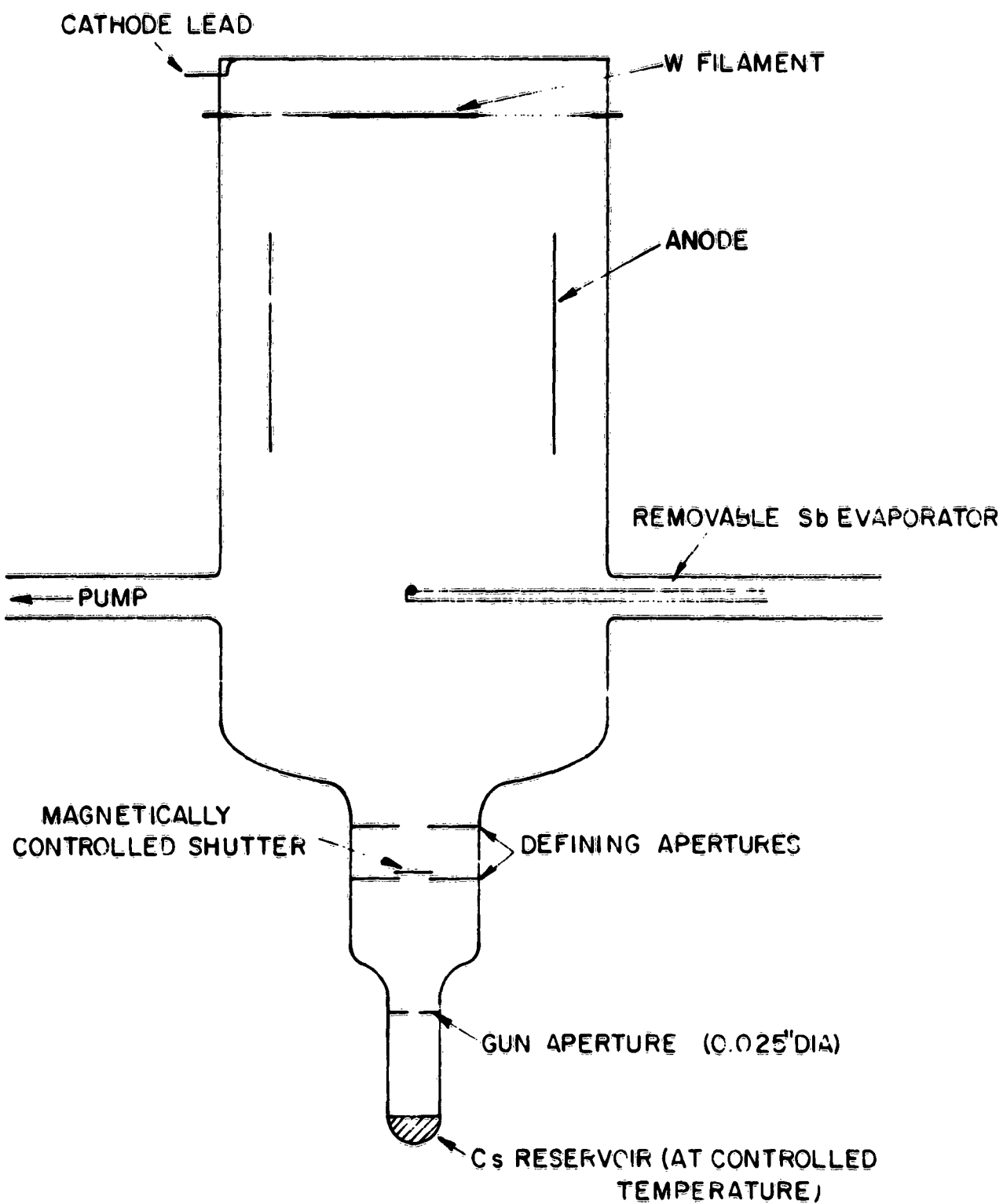


Fig. 2 Experimental Tube for Activating Photocathodes with an Atomic Beam of Cesium.

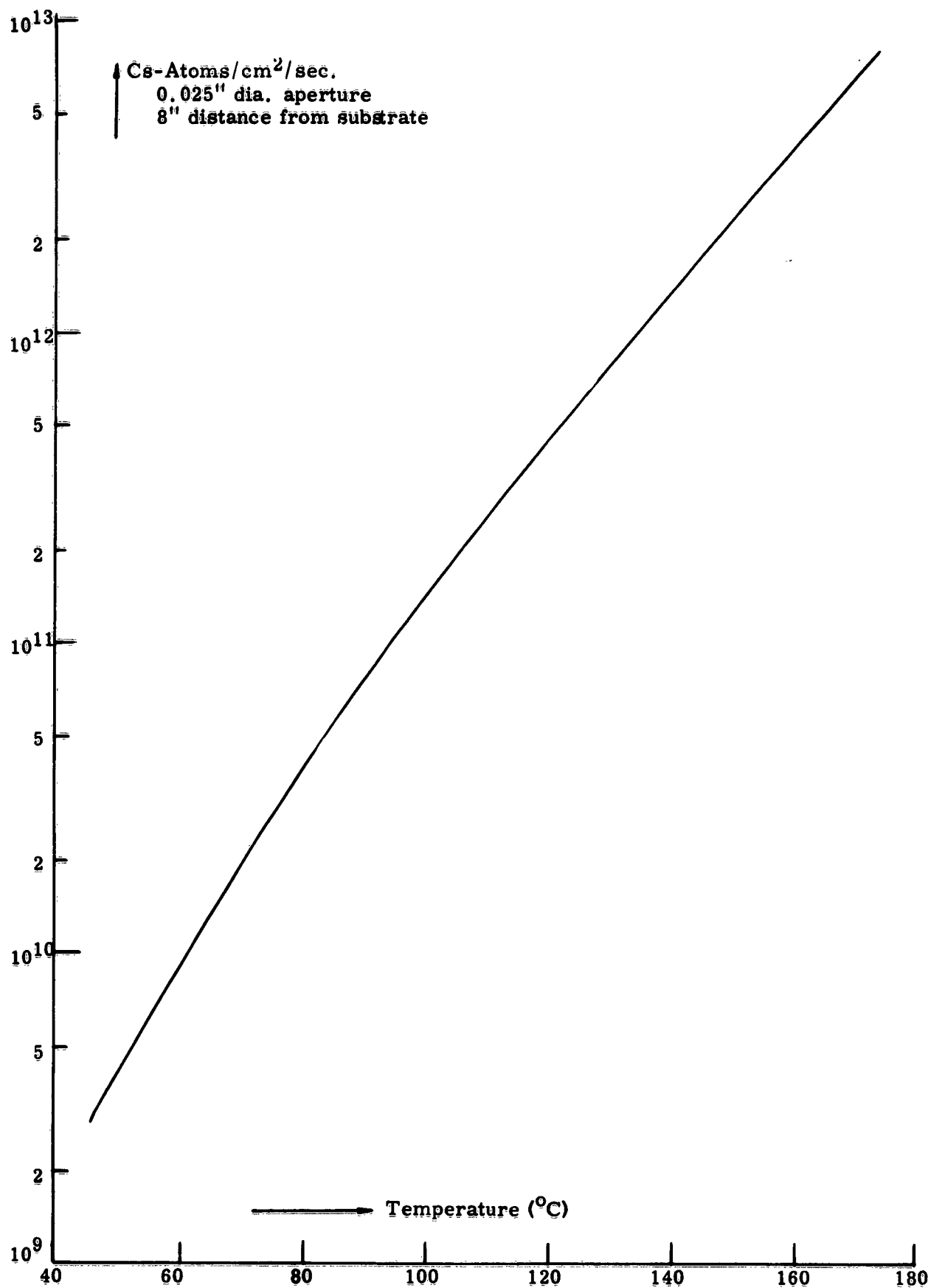


Fig. 3 Number of Cs Atoms in Atomic Beam as a Function of Temperature

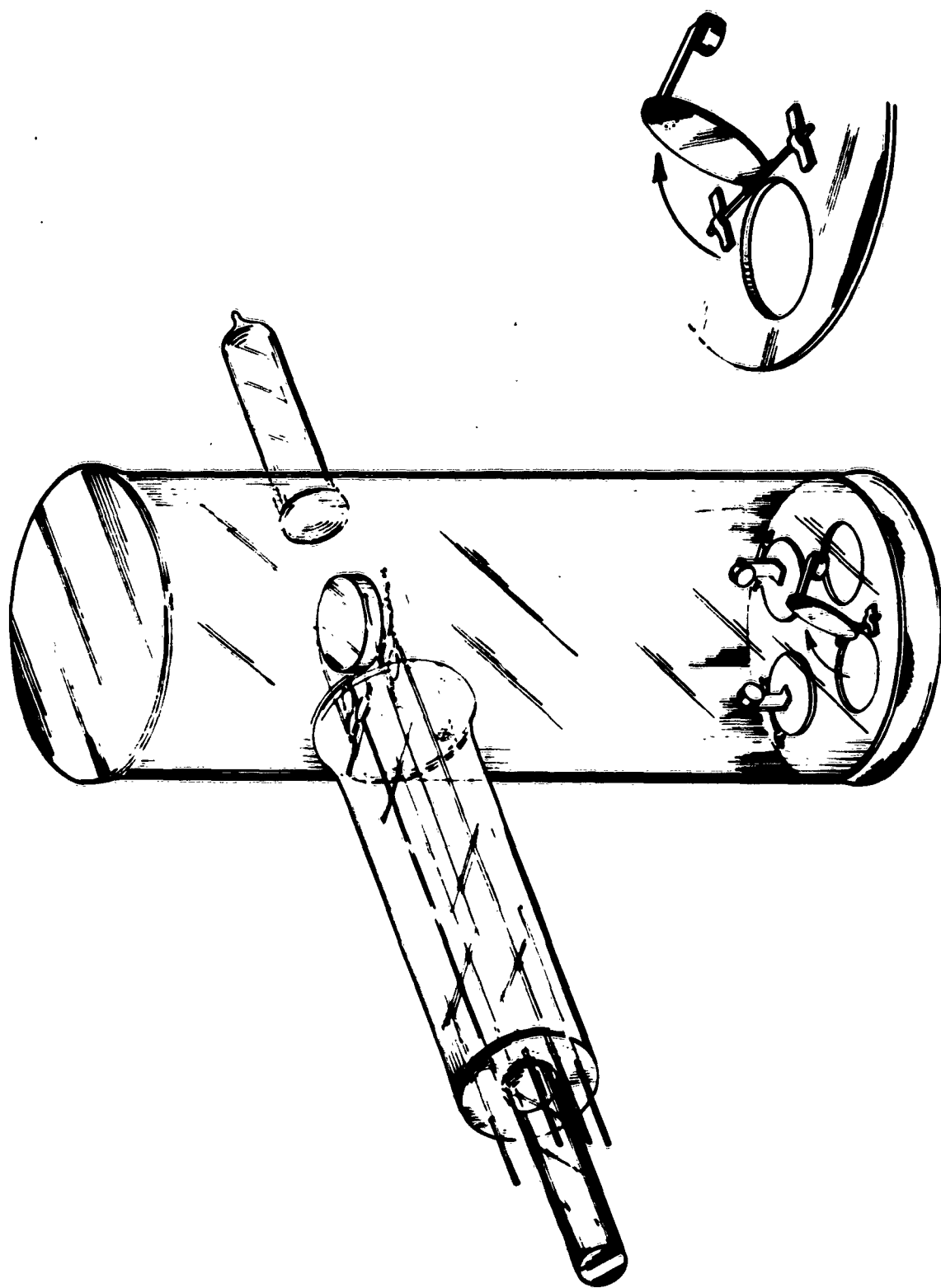


Fig. 4 Experimental Tube to Measure the Relation between Thickness and Light Transmission of an Evaporated Antimony Film

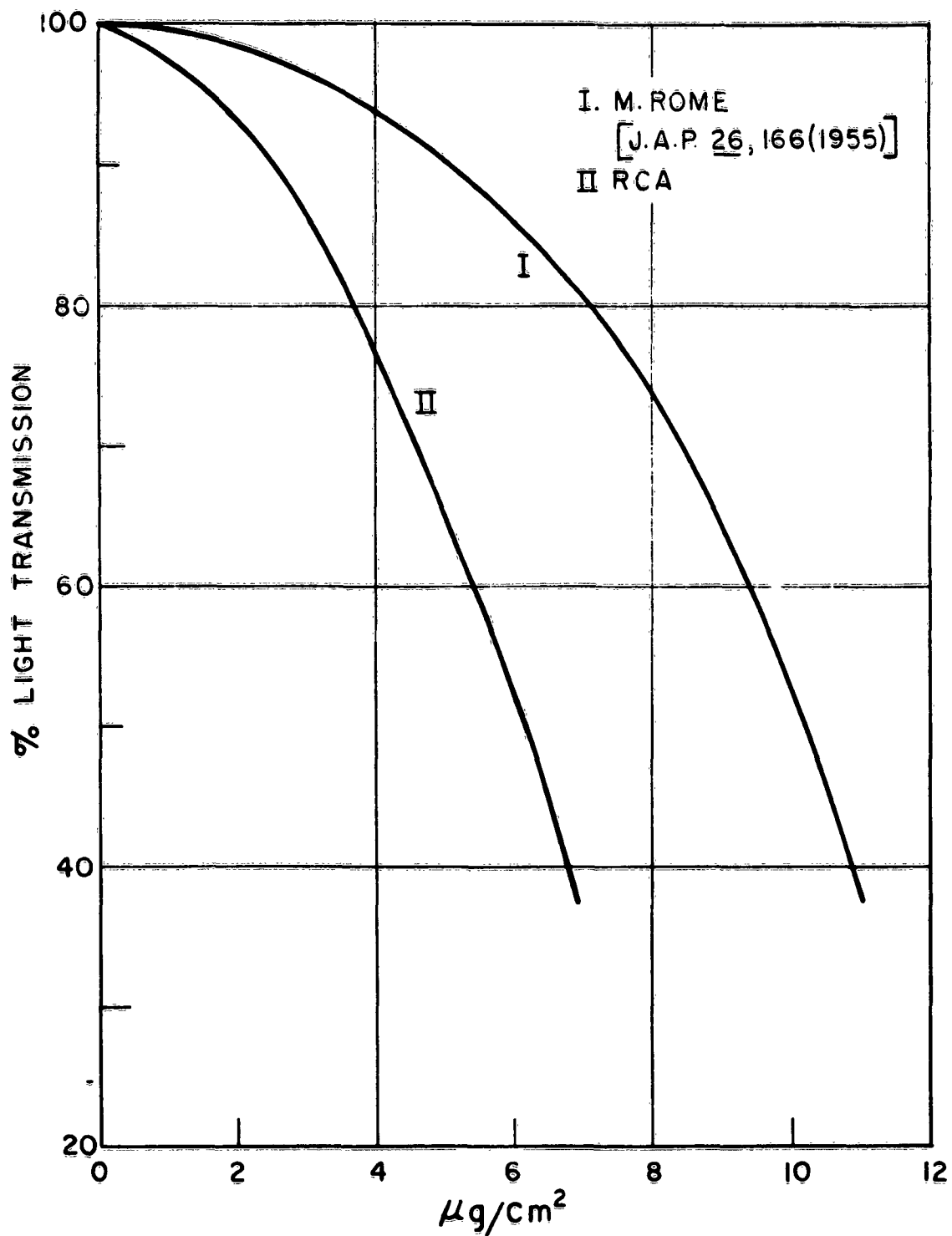
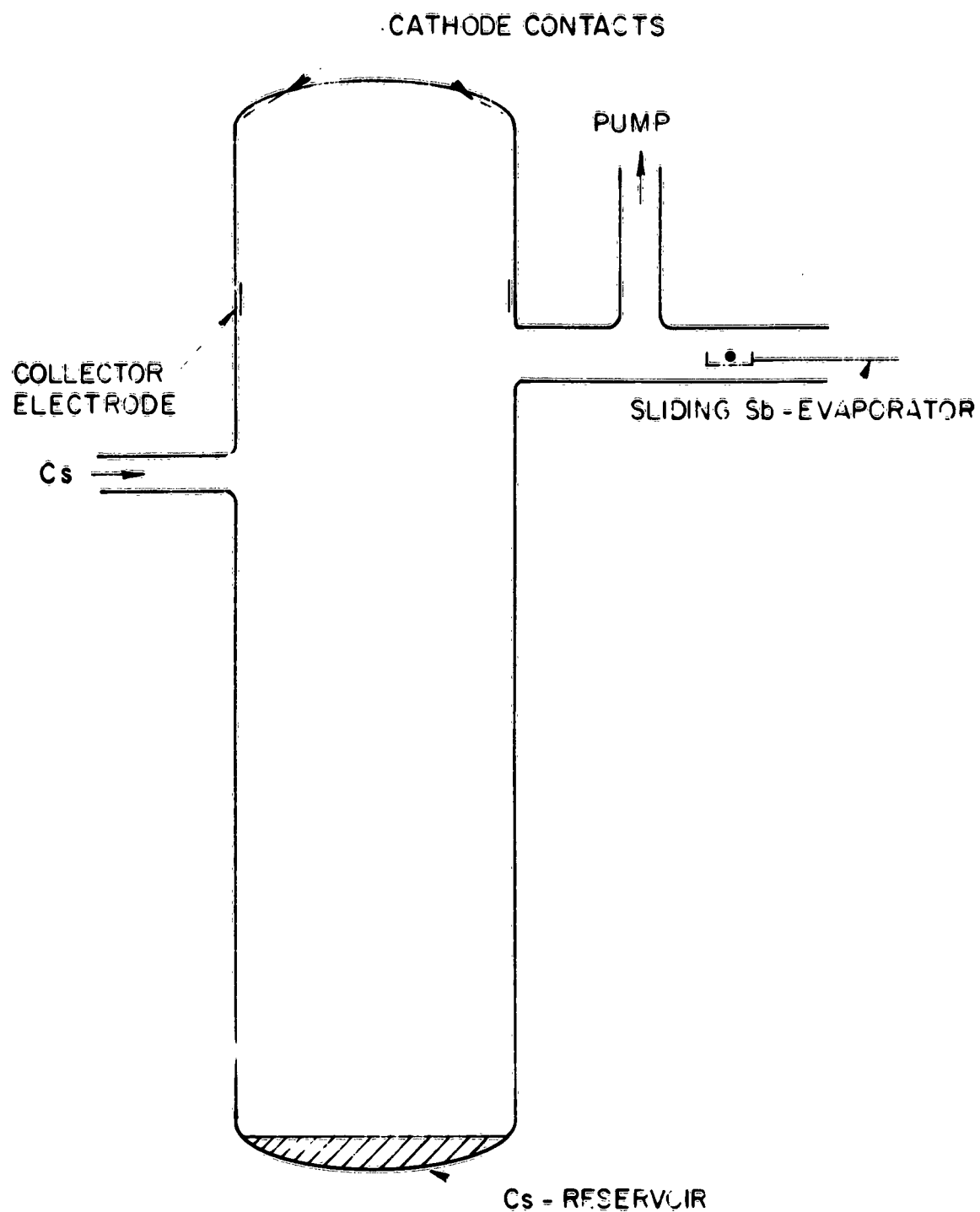


Fig. 5 Light Transmission of An Evaporated Sb Film as a Function Of Thickness



**Fig. 6 Experimental Tube for the Activation of  $\text{Cs}_3\text{Sb}$  Cathodes in an Enclosed Chamber**

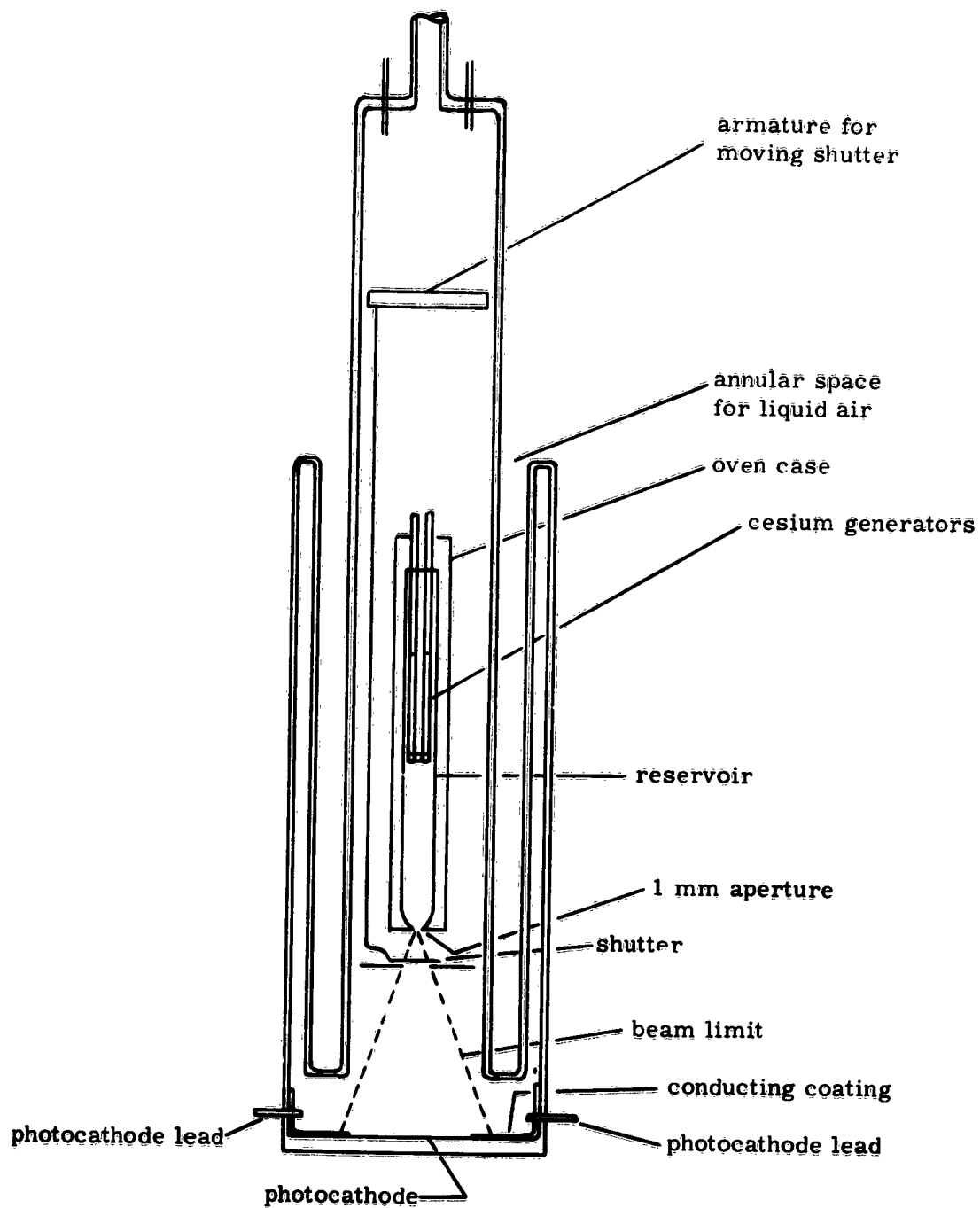


Fig. 7 Cesium Beam Tube, Second Type (half size)

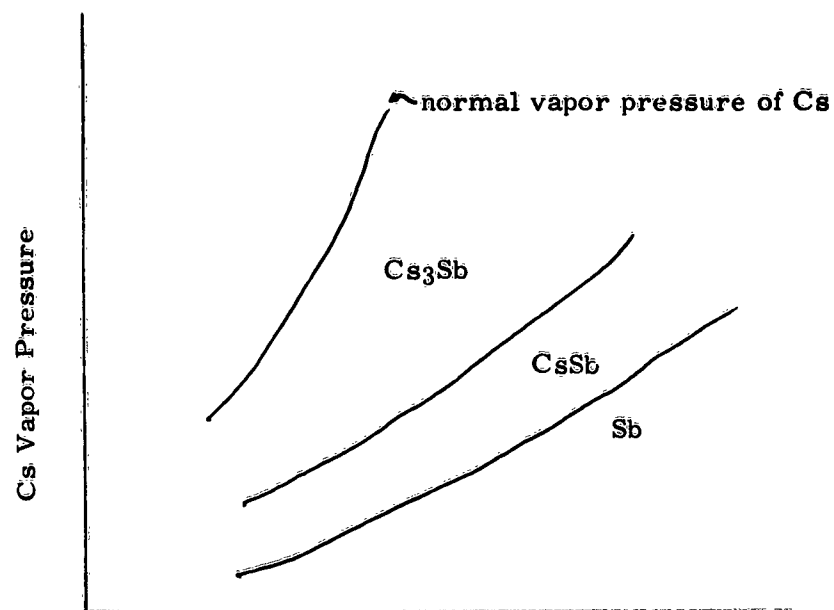


Fig. 8 Temperature

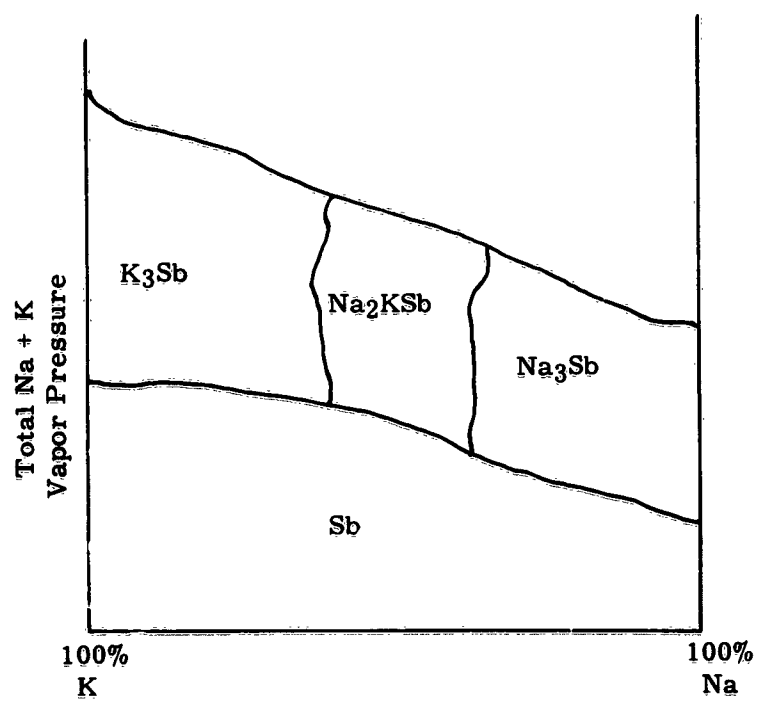


Fig. 9 Vapor Composition

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